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PRODUCTION OF SINTERED ALUMINUM NITRIDE

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Abstract

PURPOSE: To provide a method for producing sintered aluminum nitride, capable of sintering a relatively large-size molding in high yield at a low temperature of about 1700 deg.C and at the ordinary pressure.

CONSTITUTION: A method for producing sintered aluminum nitride is characterized by the following processes; With 100 pts.wt. aluminum nitride powder having 1.5 μ m-5 μ m average particle diameter, \leq 15wt.% content of fine particles of \leq 1 μ m particle diameter and \leq 3.5m²/g BET specific surface area and containing yttrium or a yttrium compound and a sulfur compound respectively in an amount of 0.5-5wt.% on yttrium oxide base and 70-500ppm on sulfur atom base, a calcium compound is admixed in an amount of 0.1-3 pts.wt. on calcium oxide base. The resultant mixture is molded and sintered in a non-oxidative atmosphere.

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Cited Reference 3

5-97523

[Title of the Invention]

ALUMINUM NITRIDE SINTERED BODY PRODUCTION METHOD

[Abstract]

Constitution: An aluminum nitride sintered body production method which comprises: adding and mixing 0.1 to 3 parts by weight of a calcium compound in terms of calcium oxide to and with 100 parts by weight of an aluminum nitride powder which has an average particle diameter of 1.5 μm to 5 μm , a content of a fine particle with a particle diameter of 1 μm or less being 15% by weight or less and a BET specific surface area being 3.5 m^2/g or less, contains 0.5 to 5% by weight of yttrium or a yttrium compound in terms of yttrium oxide and contains 70 to 500 ppm of a sulfur compound as sulfur element; forming the resultant mixture; and firing the formed body under a non-oxidizing atmosphere.

Effect: It is possible to sinter a relatively large-sized formed body at a low temperature about 1700°C in a normal pressure with a good production yield.

[Claims]

1. An aluminum nitride sintered body production method which comprises: adding and mixing 0.1 to 3 parts by weight of a calcium compound in terms of calcium oxide to and with 100 parts by weight of an aluminum nitride powder which has an average particle diameter of 1.5 μm to 5 μm , a content of a fine particle with a particle diameter of 1 μm

or less being 15% by weight or less and a BET specific surface area being 3.5 m²/g or less, contains 0.5 to 5% by weight of yttrium or a yttrium compound in terms of yttrium oxide and contains 70 to 500 ppm of a sulfur compound as sulfur element; forming the resultant mixture; and firing the formed body under a non-oxidizing atmosphere.

2. The aluminum nitride sintered body production method according to claim 1, wherein

the aluminum nitride powder which has an average particle diameter of 1.5 μ m to 5 μ m, a content of a fine particle with a particle diameter of 1 μ m or less being 15% by weight or less and a BET specific surface area being 3.5 m²/g or less, and contains 0.5 to 5% by weight of yttrium or a yttrium compound in terms of yttrium oxide and 70 to 500 ppm of a sulfur compound as sulfur element is obtained by coating an alumina powder with a yttrium compound by precipitation and subjecting the resulting powder to reductive nitridation.

[Detailed Description of the Invention]

[0001]

[Field of the Invention]

The present invention relates to an aluminum nitride sintered body production method capable of producing a relatively large-sized sintered body can be produced at a lower temperature about 1700°C as compared with a conventional method.

[0002]

[Prior Art]

Aluminum nitride (hereinafter, referred to as AlN in some cases)

has a high thermal conductivity and excellent high temperature characteristics and therefore has been attracting attention as a material usable for various applications such as an IC substrate, a packaging material, a heat sink, a furnace material, a jig for metallurgy and the like. However, as compared with oxide materials such as an alumina sintered body, it requires high sintering temperature, the production cost is high because the physical properties easily differ in the inside and the outside in the case of large-sized green bodies and the production yield is low, and its applications are limited.

[0003]

It is well known that in order to carrying out sintering at a lower temperature, a finely granular AlN powder is used, and as a sintering aid CaO is used alone or in combination with Y_2O_3 . In the case of using CaO alone, the thermal conductivity is hard to be increased and in the case of using it in combination with Y_2O_3 , supposedly attributed to that these two types of sintering aids are difficult to be dispersed evenly, the physical properties of obtained sintered bodies tend to be uneven. Especially, such tendency becomes more significant as the size of a sintered body becomes large and in the case of a large-sized sintered body production, the progress of sintering differs depending on portions and owing to uneven shrinkage, warping and cracking easily take place to result in significant decrease of the yield of products. In addition to that, with respect to a large-sized formed body, a binder is more difficult to be evaporated at inner side and thus residual carbon increases to result in retardation of sintering.

[0004]

[Problems to be Solved by the Invention]

In consideration of such circumstances, on the bases of investigations performed aiming to find a method capable of carrying out sintering at a lower temperature and producing a relatively large-sized aluminum nitride sintered body with a good production yield, inventors have found that the above-mentioned object can be accomplished entirely in the case that a raw material of a sintered body is obtained by mixing a specified amount of a calcium compound with an aluminum nitride powder previously compounded with a yttrium compound and having specified physical properties and forming and sintering the obtained mixture, thereby completed the present invention.

[0005]

[Means for Solving the Problems]

That is, the present invention provides an aluminum nitride sintered body production method comprising: adding and mixing 0.1 to 3 parts by weight of a calcium compound in terms of calcium oxide to and with 100 parts by weight of an aluminum nitride powder which has an average particle diameter of 1.5 μm to 5 μm , a content of a fine particle with a particle diameter of 1 μm or less being 15% by weight or less and a BET specific surface area being 3.5 m^2/g or less, and contains 0.5 to 5% by weight of yttrium or a yttrium compound in terms of yttrium oxide and 70 to 500 ppm of a sulfur compound as sulfur element; forming the resultant mixture; and firing the formed body under a non-oxidizing atmosphere.

[0006]

Hereinafter, the present invention will be described in detail. An aluminum nitride powder to be used for the present invention has an average particle diameter of 1.5 μm to 5 μm , preferably 2 to 4 μm . When the average particle diameter is less than 1.5 μm , the average diameter of pores formed among particles at the time of forming becomes small to deteriorate the binder removal property. On the other hand, when it exceeds 5 μm , the sintering property is deteriorated.

[0007]

Further, with respect to the aluminum nitride powder, the content of a fine particle with a particle diameter of 1 μm or less is preferably about 15% by weight or less. When a large quantity of fine particles are contained, the binder removal property is not good; therefore, the content of a fine particle with a particle diameter of 1 μm or less is desired to be low.

[0008]

The specific surface area of the aluminum nitride powder to be used for the present invention is 3.5 m^2/g or less, preferably 2.5 m^2/g or less. When the specific surface area is increased, the binder removal property is deteriorated and the content of residual carbon after sintering is increased. When the carbon content is increased, it causes an adverse effect on sintering and results in a low density of a sintered body.

[0009]

Furthermore, yttrium or a yttrium compound as a sintering aid has to be evenly contained in the aluminum nitride powder in order to obtain a sintered body with a high thermal conductivity and a high

density. The content of yttrium or the yttrium compound is preferably about 0.5 to 5% by weight in terms of yttrium oxide. When the content is smaller than 0.5% by weight, the effect as a sintering aid becomes low.

[0010]

The aluminum nitride powder containing yttrium or the yttrium compound as a sintering aid for the present invention is required to further contain 70 to 500 ppm of a sulfur compound as sulfur element. The reason is not necessarily clear but existence of sulfur improves the sintering property. When the amount of the sulfur compound as sulfur element is smaller than 70 ppm in the aluminum nitride powder, no sufficient effect can be attained and when it is larger than 500 ppm, electric properties of a sintered body such as insulating property, dielectric loss or the like become deteriorated. Further, it was found that uneven coloration, which is often observed in a conventional sintered body, is scarcely caused owing to existence of sulfur. It is supposed that the coloration unevenness is eliminated by improvement of the sintering property due to the cooperative effects with yttrium and increase of the density of the sintered body. Although coloration unevenness does not directly affect the physical properties of the sintered body, occurrence of it is not preferable since the value as a product is lowered.

[0011]

In the aluminum nitride powder used for the present invention, yttrium has to be evenly dispersed in order to promote sintering of the aluminum nitride powder. It is preferable that the yttrium and the aluminum nitride are evenly compounded in micro scale. In the case of

uneven dispersion, uneven liquid-phase formation takes place and, at the time of sintering, especially in the case of a large-sized product, the shrinkage ratio difference occurs between the inside and the outside and density becomes uneven to result in occurrence easiness of warping and cracking. An alumina-yttrium compounded powder may be obtained by compounding alumina and a yttrium compound, then subjecting to nitriding reaction. Commonly, it may be obtained by titrating dropwise an aqueous solution such as yttrium nitrate to an alumina slurry, causing neutralizing precipitation with ammonia water or the like, then precipitating and coating the yttrium compound on the surface of alumina for compounding the resultant, and after that, further carrying out conventional reductive nitridation, that is, mixing the alumina powder coated with the yttrium compound with carbon and nitriding the mixture at 1400 to 1700°.

[0012]

Sulfur may be added to the aluminum nitride powder by using a carbon powder with a high content of a sulfur compound at the time of the above-mentioned reductive nitridation or a sulfur simple substance or a sulfur-containing substance such as an aluminum sulfate powder may be added at the time of the nitriding reaction.

[0013]

In the present invention, 0.1 to 3 parts by weight of a calcium compound in terms of calcium oxide is added to and mixed with 100 parts by weight of the aluminum nitride powder having the above-mentioned physical properties and the resultant mixture is formed. Then, the

formed body is fired under a non-oxidizing atmosphere. The method of adding the calcium compound is not particularly limited; however, generally the aluminum nitride powder is dispersed in an organic solvent and the calcium compound may be added to the obtained dispersion. Although the state of the calcium compound to be used is not particularly limited, calcium carbonate, calcium nitrate and the like are preferably used. It is not preferable if the addition amount of the calcium compound to the aluminum nitride powder is less since no effect on low temperature sintering is attained, while it is not also preferable if it is too high, since the characteristics of the sintered body are adversely deteriorated.

[0014]

In general, an organic binder is added to and dispersed in the above-mentioned organic solvent in order to improve the formability. In this case, the organic solvent in which the aluminum nitride powder, the calcium compound and the binder are dispersed is well stirred to evenly mix them and then dried to obtain a composition for sintered body production.

[0015]

The mixed powder comprised of the aluminum nitride powder, the calcium compound, and optionally the binder is then formed into a desired shape and the forming method is not particularly limited. A common uniaxial press, a hydroisostatic press and the like are preferably employed. At the time of sintering, it may be carried out under a non-oxidizing atmosphere such as nitrogen.

[0016]

[Effects of the Invention]

It was found that, according to the method of the present invention described above in detail, a relatively large-sized sintered body can be produced at a low temperature around 1700°C with a good production yield by an extremely simple method involving obtaining a raw material of a sintered body by mixing a specified amount of a calcium compound with an aluminum nitride powder previously compounded with yttrium or a yttrium compound and having specified physical properties, and forming and sintering the obtained mixture; therefore, the present invention is significantly valuable in industrial fields.

[0017]

[Examples]

Hereinafter, embodiments of the present invention will be described practically with reference to Examples; however, the present invention is not to be considered as being limited by the following Examples. It is to be noted that the characteristics and properties of a powder were measured by the following devices and methods in the method of the present invention.

[0018]

(1) Average particle size and content of fine particle with particle diameter of 1 μm or less

Sedigraph E5000, manufactured by Micromeritics Co.

3 g of an aluminum nitride-type powder was dispersed in 40 g of n-butanol solution containing 0.5% by weight of Ceramo D-18 made by

Dai-Ichi Kogyo Seiyaku Co., Ltd. by ultrasonic wave for 10 minutes to carry out measurement. With respect to an alumina powder, 3 g of an alumina powder was dispersed in 47 g of an aqueous solution containing 0.1% by weight of sodium hexametaphosphate by ultrasonic wave for 10 minutes to carry out measurement.

[0019]

(2) BET specific surface area

BET specific surface area measurement device: Microsorb II, manufactured by Micromeritics Co.

[0020]

(3) Oxygen amount

Analyzer of oxygen and nitrogen in ceramic: EMGA-2800, manufactured by Horiba, Ltd.

A silicon nitride powder R-005 made by The Ceramic Society of Japan was employed as a standard sample.

[0021]

(4) Pressurized powder body density

Using a uniaxial forming die with a diameter of 20 mm, 3 g of an aluminum nitride-type powder was formed into a pellet shape by applying a pressure of 1000 kg/cm² without adding a binder or the like, and the density was calculated from the size and the weight.

[0022]

(5) Sulfur content in carbon powder and aluminum nitride-type powder

Measurement was carried out by fluorescent x-ray analyzer PW

1480 model manufactured by Phillips Co., Ltd. through employment of a calibration curve produced by carbon samples with known-content.

[0023]

Example 1

8.3 parts of Noigen EA-137 made by Dai-Ichi Kogyo Seiyaku Co., Ltd, 7.5 parts of SN-DISPERSANT 5468 made by San Nopco Ltd. and 29.4 parts of polyethylene glycol #1000 were dissolved in 1500 parts of water, and 2000 parts of an alumina powder with an average particle diameter of 0.5 μm , a BET specific surface area of 7.6 m^2/g and a Na_2O content of 0.26% were added thereto and dispersed therein by ultrasonic treatment for 30 minutes. An aqueous yttrium nitrate solution was dropwise titrated to the produced alumina slurry so as to have 49.7 parts of Y_2O_3 . The aqueous yttrium nitrate solution was adjusted so as to contain 100 g of Y as Y_2O_3 in 1000 mL. The titrated amount of yttrium nitrate was equivalent to 3% by weight in terms of yttrium oxide in an aluminum nitride-type powder to be produced. Simultaneously with the dropwise titration of yttrium nitrate, concentrated ammonia water was dropwise titrated to adjust pH to be 9.5. 82.5 parts of SN-DISPERSANT 5468 was also dropwise titrated simultaneously thereto to suppress the increase of viscosity. An alumina slurry in which thus obtained alumina was coated with yttrium hydroxide was mixed with 941 parts of a carbon powder (sulfur content is 0.26 parts by weight per 100 parts by weight of the carbon powder) using a particle granulator manufactured by Fuji Sangyo Co., Ltd. for 20 minutes. The produced mixture was dried at 120°C for 15 hours to obtain a raw material for nitriding reaction. 400

parts of the obtained raw material for nitriding reaction was loaded onto a tray made of graphite in 15 mm thickness and fired at 1660°C for 8 hours in nitrogen gas flow to carry out nitriding reaction. The temperature raising rate was controlled to be 2.6 °C/min. After the nitriding reaction, excess carbon was removed by firing at 700°C for 2 hours in air to obtain an aluminum nitride-yttrium compounded powder. The characteristics and properties of the obtained compounded powder are shown in Table 1. The oxygen amount of thus obtained compounded powder was 1.75%. The compounded powder was sintered by the following method. 0.1 parts of Ceramo D-18 made by Dai-Ichi Kogyo Seiyaku Co., Ltd. as a dispersant and 0.2 parts of acrylic resin as a binder were dissolved in 40 parts of n-butanol, and 0.36 parts of calcium carbonate and 20 parts of the compounded powder were added thereto. The resultant was subjected to ball mill mixing for 4 hours using plastic balls with iron-core having a diameter of 15 mm and then dried. The obtained mixture was press-formed into a size of 10 cm × 10 cm × 1 cm thickness by applying a pressure of 300 kg/cm² using a die, and further formed by applying a pressure of 1500 kg/cm² by rubber press to produce a formed body. The formed body was kept at 1700°C for 5 hours in a double container made of carbon in nitrogen atmosphere to carry out normal pressure sintering. The appearance (coloration unevenness) of the obtained sintered body was observed and the dispersion of the density at two points of the right and left in the upper end (1 cm portions from the end part, denoted as A and B from the left), two points of the right and left in the lower end (1 cm portions from the end part, denoted as D

and E from the left), and the center portion (denoted as C) was measured. The results are shown in Table 2.

[0024]

Comparative Example 1

8.3 parts of Noigen EA-137 made by Dai-Ichi Kogyo Seiyaku Co., Ltd., 7.5 parts of SN-DISPERSANT 5468 made by San Nopco Ltd. and 29.4 parts of polyethylene glycol #1000 were dissolved in 1500 parts of water, and 2000 parts of an alumina powder with a center particle diameter of 0.5 μm , a BET specific surface area of 7.6 m^2/g and a Na_2O content of 0.26% was added thereto and dispersed therein by ultrasonic treatment for 30 minutes. Thus obtained alumina slurry was mixed with 941 parts of a carbon powder (sulfur content is 0.05 parts by weight or less per 100 parts by weight of the carbon powder) using a particle granulator manufactured by Fuji Sangyo Co., Ltd. for 20 minutes. The produced mixture was dried at 120°C for 15 hours to obtain a raw material for nitriding reaction. 400 parts of the obtained raw material for nitriding reaction was loaded onto a tray made of graphite in 15 mm thickness and fired at 1660°C for 8 hours in nitrogen gas flow to carry out nitriding reaction. The temperature raising rate was controlled to be 2.6 °C/min. After the nitriding reaction, the reaction product was pulverized by a ball mill for about 3 Hr and fired at 700°C for 2 hours in air to remove excess carbon and obtained an aluminum nitride-type powder. The characteristics and properties of the obtained aluminum nitride-type powder are shown in Table 1. Additionally, the oxygen amount of the obtained aluminum nitride-type powder was 1.25%. At

the time of sintering, the obtained powder was sintered by the same method as that of Example 1, except that a mixed powder obtained by mixing 0.6 parts of yttrium oxide (the addition ratio of yttrium oxide to the aluminum nitride powder was 3.0% by weight) with 19.4 parts of the aluminum nitride powder obtained in the above-mentioned method was used in place of the aluminum nitride-yttrium compounded powder of Example 1 and the dispersion of density was investigated in the same manner. The results are shown in Table 2.

[0025]

Comparative Example 2

Sintering was carried out by the same method as that of Comparative Example 1, except that a commercially available powder with a large particle diameter shown in Table 1 was used in place of the aluminum nitride powder of Comparative Example 1. The sintering density was measured and the dispersion of density was investigated in the same manner. The results are shown in Table 2. As being made clear from the results, the sintering density was 3.14 g/cc on the average and did not reach 3.20 g/cc showing insufficient promotion of sintering.

[0026]

Comparative Example 3

Sintering was carried out using the same compounded powder as that of Example 1 by the same method as that of Example 1, except that no calcium compound was added. The sintering density was 2.74 g/cc on the average, showing that no sintering was promoted.

[0027]

[Table 1]

	Average particle diameter (μm)	1 μm or less (%)	Specific surface area (m^2/g)	Sulfur content (ppm)	Note
Example 1	2.3	7	2.2	170	Oxygen: 1.75%
Comparative Example 1	1.2	35	3.7	10	Oxygen: 1.25%
Comparative Example 2	2.4	5	2.3	40	Oxygen: 0.85%



[0028]

[Table 2]

Sintering density: unit (g/cc)

	A	B	C	D	E	Coloration unevenness
Example 1	3.25	3.24	3.24	3.24	3.24	Not observed
Comparative Example 1	3.26	3.23	3.16	3.24	3.23	Observed
Comparative Example 2	3.15	3.17	3.09	3.13	3.17	-

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(54) 【発明の名称】 窒化アルミニウム焼結体の製造方法

(57) 【要約】

【構成】 平均粒径1.5 μm ~5 μm 、粒径1 μm 以下の微粒含有量が15重量%以下、BET比表面積が3.5 m^2/g 以下で、イットリウム或いはイットリウム化合物を酸化イットリウムに換算して0.5~5重量%含有し、かつ硫黄化合物を硫黄元素として70~500 ppm含有してなる窒化アルミニウム粉末100重量部にカルシウム化合物を酸化カルシウムに換算して0.1~3重量部添加、混合、成形した後、非酸化性雰囲気下で焼成することを特徴とする窒化アルミニウム焼結体の製造方法。

【効果】 常圧、1700℃程度の低温で比較的大型の成形体を製品歩留りよく焼結することができる。

【特許請求の範囲】

【請求項1】 平均粒径1.5 μ m \sim 5 μ m、粒径1 μ m以下の微粒含有量が15重量%以下、BET比表面積が3.5m²/g以下で、イットリウムまたはイットリウム化合物を酸化イットリウムに換算して0.5 \sim 5重量%含有し、かつ硫黄化合物を硫黄元素として70 \sim 500ppm含有してなる窒化アルミニウム粉末100重量部にカルシウム化合物を酸化カルシウムに換算して0.1 \sim 3重量部添加、混合、成形した後、非酸化性雰囲気下で焼成することを特長とする窒化アルミニウム焼結体の製造方法。

【請求項2】 アルミナ粉末にイットリウム化合物を析出被覆した後、還元窒化することにより得た平均粒径1.5 μ m \sim 5 μ m、粒径1 μ m以下の微粒含有量が15重量%以下、BET比表面積が3.5m²/g以下で、イットリウムまたはイットリウム化合物を酸化イットリウムに換算して0.5 \sim 5重量%含有し、かつ硫黄化合物を硫黄元素として70 \sim 500ppm含有してなる窒化アルミニウム粉末を用いることを特徴とする請求項1記載の窒化アルミニウム焼結体の製造方法。

【発明の詳細な説明】

【0001】

【産業上の利用分野】本発明は、比較的大型の焼結体を約1700 $^{\circ}$ C程度の従来に比較しより低い温度で焼結し得る窒化アルミニウム焼結体の製造方法に関する。

【0002】

【従来の技術】窒化アルミニウム（以下AlNと称する場合がある。）は高い熱伝導度を有し、高温特性もよく、IC基板・パッケージ材料、ヒートシンク、炉材、冶金用治具など様々な用途材料として注目されている。しかしながらアルミナ焼結体等の酸化物材料に比べると焼結温度が高く、また大型成形品は内部と外部の物性差が生じ易く製品歩留りが悪いと製造コストが高くなり、用途も限定されていた。

【0003】より低温で焼結させるためには微粒のAlN粉を用い、焼結助剤としてCaOを単独、あるいはY₂O₃との組合せで用いることが公知である。CaO単独で用いる場合には熱伝導度が上がりにくく、Y₂O₃との組合せで用いる場合には二種の焼結助剤を均一に分散し難いため得られる焼結体の物性にバラつきを生じ易い傾向にある。特にこの傾向は大型の焼結体ほど大きく、大型の焼結体を製造する際には、場所により焼結の進行状態が異なり、不均一な収縮によりソリ、割れが発生し易く、製品の歩留りが著しく悪化する。加えて大型成形体は内部ほどバインダーが揮散し難く、残留炭素が多くなるため焼結が進まないとの不都合を有する。

【0004】

【発明が解決しようとする課題】かかる事情に鑑み、本発明者らはより低温での焼結が可能で、比較的大型の窒化アルミニウム焼結体を歩留りよく製造できる方法を見

いだすことを目的とし鋭意検討した結果、予めイットリウム化合物を複合した特定物性を有する窒化アルミニウム粉末に特定量のカルシウム化合物を混合し焼結体原料となし、これを成形、焼結する場合には上記目的がすべて達成し得ることを見だし本発明を完成するに至った。

【0005】

【課題を解決するための手段】すなわち本発明は、平均粒径1.5 μ m \sim 5 μ m、粒径1 μ m以下の微粒含有量が15重量%以下、BET比表面積が3.5m²/g以下で、イットリウムまたはイットリウム化合物を酸化イットリウムに換算して0.5 \sim 5重量%含有し、かつ硫黄化合物を硫黄元素として70 \sim 500ppm含有してなる窒化アルミニウム粉末100重量部にカルシウム化合物を酸化カルシウムに換算して0.1 \sim 3重量部添加、混合、成形した後、非酸化性雰囲気下で焼成することを特長とする窒化アルミニウム焼結体の製造方法を提供する。

【0006】以下本発明を詳細に説明する。本発明に使用する窒化アルミニウム粉末は、平均粒径1.5 μ m \sim 5 μ mであり、好ましくは2 \sim 4 μ mである。平均粒径が1.5 μ m未満では成形時の粒子間に生じる平均のポア径が小さくなり脱バインダー性が悪くなる。他方5 μ mを越えると焼結性が悪くなる。

【0007】また窒化アルミニウム粉末は、粒径1 μ m以下の微粒含有量は約15重量%以下であることが好ましい。微粒が多く含まれている場合にはバインダー除去性が良好ではないので、特に粒径1 μ m以下の微粒含有量が少ないことが望まれる。

【0008】本発明に使用する窒化アルミニウム粉末の比表面積は3.5m²/g以下、好ましくは2.5m²/g以下である。比表面積が大きくなると脱バインダー性が悪くなり焼成後の残留カーボン含有量が多くなる。カーボン含有量が多くなると焼結に悪影響を及ぼし、焼結体密度が低くなる。

【0009】さらに窒化アルミニウム粉末中には、熱伝導度の高い緻密な焼結体を得る為に焼結助剤であるイットリウム或いはイットリウム化合物が均一に含有されていなければならない。イットリウム或いはイットリウム化合物の含有量は酸化イットリウムに換算して約0.5 \sim 約5重量%の範囲が好適である。該含有量が0.5重量%より少ない場合には焼結助剤としての効果が低い。

【0010】焼結助剤であるイットリウム或いはイットリウム化合物を含有した本発明に用いる窒化アルミニウム粉末は、さらに硫黄化合物を硫黄元素として70 \sim 500ppm含有されていることが必要である。理由は詳らかではないが硫黄が存在することにより焼結性が改善される。窒化アルミニウム粉末に対して硫黄化合物が硫黄元素として70ppmより少ない場合には十分な効果は認められず、500ppmより多い場合には焼結体は

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絶縁性や誘電損失等の電氣的性質が低下する。また硫黄が含有されていることにより、焼結体に従来よく見られた色ムラが生じにくいことが判明した。これはイットリウムとの相乗効果により焼結性が改善され、焼結体密度が大きくなることにより色ムラが消失するものと推定される。色ムラは焼結体の物性に直接影響するものではないが、色ムラの発生は商品としての価値を減ずるもので好ましくない。

【0011】本発明に用いる窒化アルミニウム粉末は焼結を促進させるためイットリウムが均一に窒化アルミニウム中に分散していなければならない。好ましくは窒化アルミニウムとミクロ的な領域で均一に複合されていることが推奨される。不均一であれば液相の生成が不均一となり焼結に際し、特に大型品の場合、内部と外部の収縮率の差、密度のバラつきなどを生じ、ソリ、割れ等を生じ易くなる。窒化アルミニウムとイットリウムの複合粉末を得るには、アルミナとイットリウム化合物を複合させた後窒化反応せしめればよく、通常、アルミナスラリー中へ硝酸イットリウムなどの水溶液を滴下し、アンモニア水などで中和析出させ、アルミナの表面にイットリウム化合物を析出被覆し、複合化させ、この後通常の還元窒化法、即ちイットリウム化合物で被覆されたアルミナ粉末をカーボンと混合し、1400℃～1700℃の温度で窒化し、窒化アルミニウム-イットリウム複合粉末とすればよい。

【0012】窒化アルミニウム粉末中への硫黄の添加は上記還元窒化時に使用するカーボン粉末として硫黄化合物の含有量の高いものを用いてもよいし、窒化反応にさいし硫黄単体或いは硫酸アルミニウム粉末等の硫黄含有物質を添加してもよい。

【0013】本発明においては上記物性を有する窒化アルミニウム粉末100重量部にカルシウム化合物を酸化カルシウムに換算して0.1～3重量部添加、混合、成形した後、非酸化性雰囲気下で焼成する。これらカルシウム化合物の添加方法は特に制限されないが、窒化アルミニウム粉末を通常有機溶媒に分散し、カルシウム化合物を添加すればよい。適用するカルシウム化合物の形態は特に限定はないが、炭酸カルシウム、硝酸カルシウムなどが好んで用いられる。窒化アルミニウム粉末に対するカルシウム化合物の添加量が少ないと低温焼結の効果がなく、多いと焼結体の特性が損なわれるので好ましくない。

【0014】また通常は成形性を良好ならしめるため有機バインダーを上記有機溶媒に分散添加する。この場合には窒化アルミニウム粉末-カルシウム化合物-バインダーが分散した有機溶媒をよく攪拌し、均一に混合した後、乾燥し、焼結体製造用組成物とすればよい。

【0015】窒化アルミニウム粉末とカルシウム化合物、必要に応じてバインダーを混合した粉末は次に成形を行い、所望の形状に成形するが、成形法については特

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に限定はない。通常の1軸プレス、静水圧プレスなどが好んで使用される。焼結に際しては窒素などの非酸化性雰囲気下で行えばよい。

【0016】

【本発明の効果】以上詳述した本発明方法によれば予めイットリウム或いはイットリウム化合物を複合した特定物性を有する窒化アルミニウム粉末に特定量のカルシウム化合物を混合し焼結体原料となし、これを成形、焼結するという極めて簡単な方法で、比較的大型の焼結体を1700℃程度の低温で歩留りよく製造できることを見出したものであり、その工業的価値は頗る大である。

【0017】

【実施例】以下、実施例により本発明の内容を具体的に説明するが、本発明は下記実施例により制限されるものではない。なお、本発明方法において粉末の特性は以下の装置および方法により測定した。

【0018】①平均粒径及び粒径1μm以下の微粒含有量

；マイクロメリティックス社製 セディグラフ E5000

窒化アルミニウム質粉末3gを、第一工業製薬株式会社性セラモD-18の0.5重量% n-ブタノール溶液40gを超音波で10分間処理することにより分散させて測定した。アルミナ粉末については、アルミナ粉末3gをヘキサメタリン酸ナトリウムの0.1重量%水溶液47gを超音波で10分間処理することにより分散させて測定した。

【0019】②BET比表面積

マイクロメリティックス社製 BET比表面積測定装置 マイクロソープII

【0020】③酸素量

堀場製作所製 セラミックス中酸素窒素分析装置 EMGA-2800

標準試料は財団法人日本セラミックス協会製 窒化ケイ素粉末R-005を使用した。

【0021】④圧粉体密度

直径20mmの一軸成形金型を使用し、窒化アルミニウム質粉末3gをバインダー等の添加なしで1000kg/cm²の圧力を加えてペレット状に成形し、寸法と重さから密度を算出した。

【0022】⑤カーボン粉末および窒化アルミニウム質粉末中の硫黄含有量

；フィリップス社製蛍光X線分析装置PW1480型を使用し、既知の値のカーボン試料を用い検量線を作成し求めた。

【0023】実施例1

水1500部に第一工業製薬株式会社製ノイゲンEA-137を8.3部、サンノブコ社製SN-DISPER SANT5468を7.5部、ポリエチレングリコール#1000を29.4部溶解させ、平均粒径が0.5μ

で、BET比表面積 $7.6\text{ m}^2/\text{g}$ でNa:O含有量が0.26%のアルミナ粉2000部を加えて、30分間の超音波処理により分散させた。生成したアルミナスラリー中に硝酸イットリウム水溶液をY:O₃として49.7部となるよう滴下した。硝酸イットリウム水溶液中にはYが1000ml中にY:O₃として100g含まれるように調整した。硝酸イットリウムの滴下量は、生成する窒化アルミニウム質粉末に対し酸化イットリウムに換算して3重量%に相当する。硝酸イットリウムの滴下と同時に濃アンモニア水を滴下し、PHが9.5になるように調整し、またSN-DISPER SANT 5468も82.5部同時に滴下し、粘度上昇を抑えた。このようにして得られたアルミナに水酸化イットリウムを被覆したアルミナスラリーとカーボン粉末(硫黄含有量がカーボン粉末100重量部に対し0.26重量部)941部とを富士産業株式会社製パーティカルグラニュレータを使用して20分間混合し、生成した該混合物を120℃で15時間乾燥させて窒化反応用原料を得た。該窒化反応用原料400部をグラファイト製のトレー上に暑さ15mmとなるように仕込み、窒素気流中1660℃にて8時間焼成し窒化反応を行った。昇温速度は2.6℃/分とした。窒化反応後、空気中で700℃にて2時間焼成し、余剰カーボンを除去し、窒化アルミニウム-イットリウム複合粉末を得た。得られた複合粉末の特性を表1に示す。また得られた複合粉末の酸素量は1.75%であった。この複合粉末の焼結を以下の方法で行った。n-ブタノール40部に、分散剤として第一工業製薬株式会社製セラモD-18を0.1部、バインダーとしてアクリル樹脂を0.2部溶解し、炭酸カルシウム0.36部、複合粉末20部を添加して、直径15mmの鉄芯入りプラスチックボールを使用して、ボールミル混合を4時間行った後に乾燥させた。該混合物を金型を使用して300kg/cm²の圧力で10cm×10cm×厚さ1cmの大きさにプレス成形し、さらにラバープレスにより1500kg/cm²の圧力で成形を行い成形体を作製した。該成形体を窒素雰囲気中カーボン製の二重容器中で、1700℃で5時間保持して常圧焼結を行った。この焼結体の外観(色ムラ)を観察し、焼結体の上端左右2ヶ所(端部より各1cmの部分、向かって左よりA、Bと記す)、下端左右2ヶ所(端部より各1cmの部分、向かって左よりD、Eと記す)、及び中央部(Cと記す)の密度のバラつきを測定した。その結果を表2に示す。

【0024】比較例1

水1500部に第一工業製薬株式会社製ノイゲンEA-137を8.3部、サンノブコ社製SN-DISPER SANT 5468を7.5部、ポリエチレングリコール#1000を29.4部溶解させ、中心粒径が0.5μで、BET比表面積 $7.6\text{ m}^2/\text{g}$ でNa:O含有量が0.26%のアルミナ粉2000部を加えて、30分間の超音波処理により分散させた。このようにして得られたアルミナスラリーとカーボン粉末(硫黄含有量がカーボン粉末100重量部に対し0.05重量部以下)941部とを富士産業株式会社製パーティカルグラニュレータを使用して20分間混合し、生成した該混合物を120℃で15時間乾燥させて窒化反応用原料を得た。該窒化反応用原料400部をグラファイト製のトレー上に暑さ15mmとなるように仕込み、窒素気流中1660℃にて8時間焼成し窒化反応を行った。昇温速度は2.6℃/分とした。窒化反応後、反応物をボールミルで約3Hr解砕し、空気中で700℃にて2時間焼成し、余剰カーボンを除去し、窒化アルミニウム質粉末を得た。得られた窒化アルミニウム質粉末の特性を表1に示す。また得られた窒化アルミニウム質粉末の酸素量は1.25%であった。なお焼結に際して実施例1の窒化アルミニウム-イットリウム複合粉末の代わりに上記方法で得た窒化アルミニウム粉末19.4部に酸化イットリウム0.6部(窒化アルミニウム粉末に対する酸化イットリウムの添加割合は3.0重量%である)を添加混合した粉末を使用した他は全く実施例1と同様な方法により焼結し、同様な方法で密度のバラつきを調べた。その結果を表2に示す。

【0025】比較例2

比較例1で用いた窒化アルミニウム粉末の代わりに、市販の表1に示す粒径の大きい粉末を用いた他は比較例1と全く同様の方法で焼結した。焼結密度を測定し同様の方法で密度のバラつきを調べた。その結果を表2に示す。これより明らかなように焼結密度が平均3.14g/ccで3.20g/ccに達せず焼結が充分進んでいなかった。

【0026】比較例3

実施例1と同様の複合粉末を用い、カルシウム化合物の添加を行わず、その他は同様の方法で焼結した。焼結密度は平均2.74g/ccで焼結していなかった。

【0027】

【表1】

	平均粒径 (μ)	1 μ 以下 (%)	比表面積 (m^2/g)	硫黄含量 (ppm)	備 考
実施例 1	2.3	7	2.2	170	酸素1.75%
比較例 1	1.2	35	3.7	10	酸素1.25%
比較例 2	2.4	5	2.3	40	酸素0.85%

【0028】

位 (g/cc)

【表2】

焼結密度

単 10

	A	B	C	D	E	色 ムラ
実施例 1	3.25	3.24	3.24	3.24	3.24	なし
比較例 1	3.26	3.23	3.16	3.24	3.23	あり
比較例 2	3.15	3.17	3.09	3.13	3.17	—